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Vaporization of molecular titanium coordination compounds—a structural–thermochemical approach

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Abstract

A semi-empirical structural–thermochemical approach was employed to study the vaporization properties of new molecular titanium coordination compounds. Examination of intramolecular steric shielding of individual atoms, and analysis of intermolecular close contacts, identified which groups of atoms in the molecules were important. Evaporation enthalpies were calculated by summing the contributions from the individual groups. Addition of the measured melting enthalpies gave sublimation enthalpies agreeing closely with data determined experimentally using high temperature mass spectrometry. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The metal organic chemical vapour deposition (MOCVD) method for producing dielectric thin films has attracted attention due to its good conformality and scalability. The success of the method depends on the volatility and stability of the precursor complexes. In designing new precursor complexes, it would be advantageous to be able to predict their properties in order to tailor the design to maximum effect. Ideally, in multicomponent systems there should be a good match between the thermochemical properties of the individual components. We have chosen the recently prepared titanium complexes [1] bis[(μ-*N*-methyldiethoxoamine)bis(2,3-dimethyl-2,3-butanediolate)-titanium] $[Ti(MDEA)(OC(CH_3)_2C(CH_3)_2O)]_2$ (I), and bis[(μ-*N*-ethyldiethoxoamine)bis(3,4-diethyl-3,4-hexanediolate)titanium] $[Ti(MDEA)(OC(C_2H_5)_2C(C_2H_5)_2O)]_2$ (II) (MDEA represents the methyldiethoxoamine ligand $(–OCH_2CH_2)_2NCH_3$) as model compounds for this study. X-ray structural data showed that these substances crystallize as dimers (Fig. 1a and b). They sublime at (150 ± 20) °C/10^{-2} mmHg, making it possible to study their evaporation properties using high temperature mass spectrometry. From the determination of the vaporization properties of complexes I and II by measurements of structural and thermochemical data we propose to develop a model to predict the vaporization properties in analogous compounds of titanium and other

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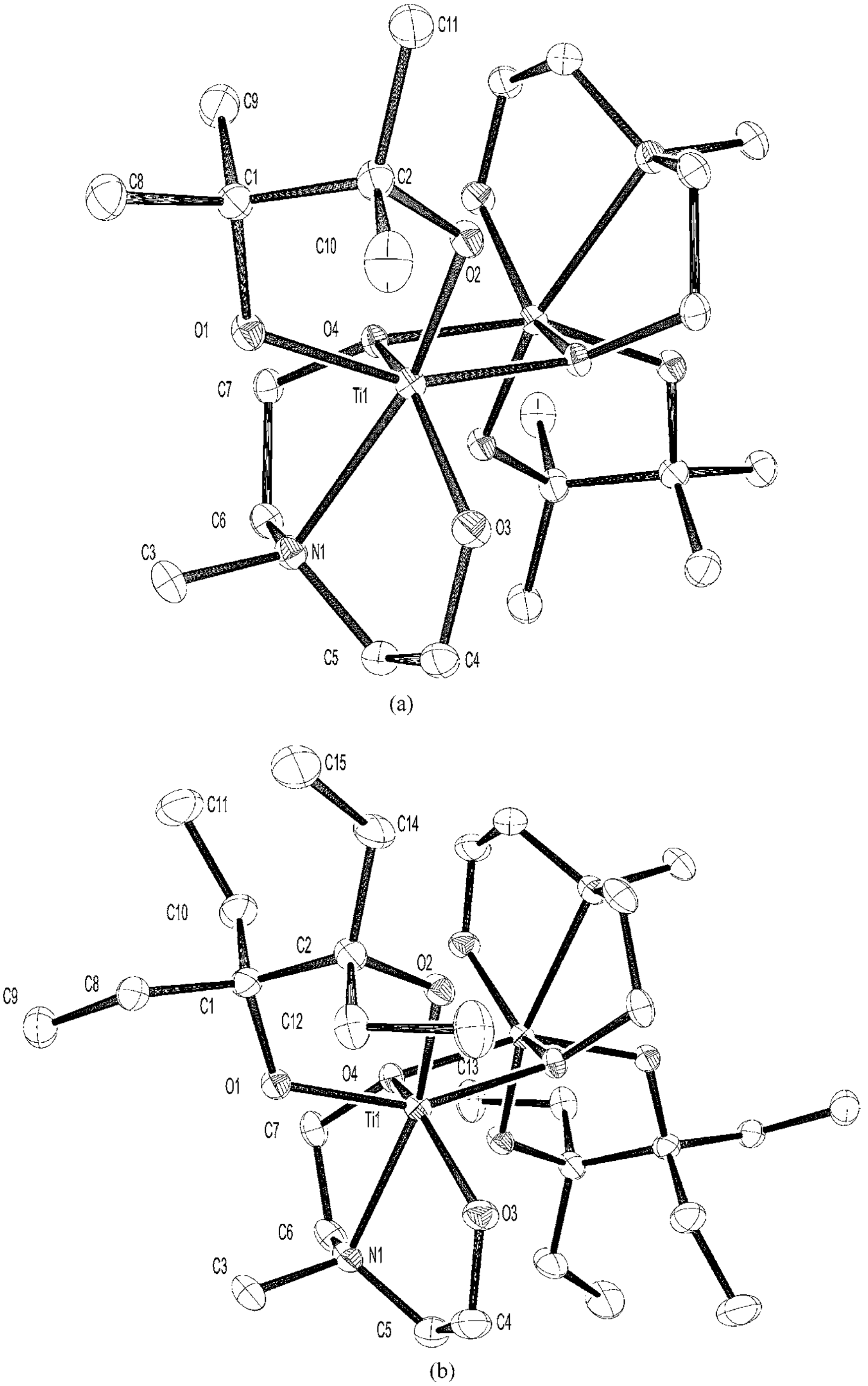


Fig. 1. (a) Molecular structure of $[Ti(MDEA)(OC(CH_3)_2C(CH_3)_2O)]_2$ (I); (b) molecular structure of $[Ti(MDEA)(OC(C_2H_5)_2C(C_2H_5)_2O)]_2$ (II).

elements. Here we describe the investigation of the vaporization processes for I and II and the analysis of the obtained results by application of the structural–thermochemical approach [2].

2. Experimental section

2.1. Measurement of melting enthalpies

2.1.1. Quantitative differential thermal analysis

Thermogravigrams of substances I and II (a charge of about 30 mg) were recorded on an F. Paulik, J. Paulik, L. Erdey device in the temperature range 20–500 °C with the heating rate of 10 °C/min. The melting point was observed to be 245 ± 5 °C for I and 177 ± 5 °C for II. The melting enthalpies $\Delta_m H^\circ$ of I and II were calculated to be 42 ± 5 and 46 ± 2 kJ/mol, respectively.

2.1.2. Differential scanning calorimetry

It was measured on a Rheometrics STA-1500 instrument under a nitrogen atmosphere confirmed the $\Delta_m H^\circ$ values as 43 ± 5 and 47 ± 2 kJ/mol, respectively. In air, some decomposition was observed on heating above 250 °C and was most pronounced at ca. 300 °C.

2.2. High temperature mass spectrometry

The experimental data were obtained by the Knudsen effusion method with mass spectral monitoring of the gas-phase composition using a USSR Academy of Sciences MS 1301 mass spectrometer. A standard nickel effusion cell was a source of the molecular beam, with the ratio of the evaporation area to the effusion area being ≈600. The temperature was measured by a platinum/platinum–rhodium thermocouple and was held constant with an accuracy of ±1 °C. The ions detected were the products of dissociative ionisation of the molecules $[Ti(MDEA)(OC(CH_3)_2C(CH_3)_2O)]_2$ and $[Ti(MDEA)(OC(C_2H_5)_2C(C_2H_5)_2O)]_2$, although no molecular ions were detected in either case. Both compounds examined sublimed congruently as evidenced by the maintenance of stable current intensities throughout each experiment, and the lack of non-volatile residues remaining in the effusion cell at the end of the runs. Saturated vapor pressures of I and II were calculated using the Hertz–Knudsen equation as 6.8×10^{-7} atm at 410 K, and 1.8×10^{-7} atm at 430 K, respectively.

2.2.1. $[Ti(MDEA)(OC(CH_3)_2C(CH_3)_2O)]_2$ (I)

The measurements were carried out in the temperature range 359–422 K. At $T = 416$ K and $U_{\text{ioniz}} = 98$ V, the mass spectrum of the gas phase over I consists mainly of the following ions with the relative current intensities shown in parentheses: $[Ti_2(MDEA)_2O_2]^+$, $m/z = 362$ (100%), $[Ti(MDEA)(OC(CH_3)_2C(CH_3)_2O)]_2^+$, $m/z = 446$ (20%) and $[Ti(MDEA)(OC(CH_3)_2)]^+$, $m/z = 112$ (14%). The maximum mass-to-charge ratio ion observed corresponded to $[[Ti(MDEA)(OC(CH_3)_2C(CH_3)_2O)]_2$-28 Da$]^+$, $m/z = 534$ (1.5%).

Studies of the temperature dependencies of the ion current $I([Ti_2(MDEA)_2O_2]^+)$ allowed the standard sublimation enthalpy of I to be obtained by the second law method using the least-squares procedure (Table 1). The equation of the temperature dependence of the saturated vapor pressure of I is represented by

$$\ln(p\,[\text{atm}]) = (27.92 \pm 0.33) - \frac{17267 \pm 210}{T}, \quad T = 359-422\,\text{K}$$

Table 1
The standard sublimation enthalpy of I

Run number	Number of points	Temperature range (K)	T (K)	$\Delta_s H^\circ(T)$[a] (kJ/mol)
1	22	359–422	391	143.0 ± 1.9
2	22	359–422	391	142.8 ± 1.3
3	22	359–422	391	143.2 ± 0.7
4	22	359–422	391	145.2 ± 0.9
Recommended value				143.6 ± 1.8[b]

[a] The errors are standard errors of the least-squares method.

[b] The recommended value is the average of the individual runs, $T = 391$ K; the error is the 95% confidence interval for the mean.

Table 2
The standard sublimation enthalpy of II

Ion	Run number	Number of points	Temperature range (K)	T (K)	$\Delta_s H^\circ(T)^a$ (kJ/mol)
A^+	1	23	370–437	404	155.4 ± 0.7
A^+	2	23	370–437	404	152.5 ± 0.5
A^+	3	22	370–438	404	155.9 ± 1.0
D^+	4	17	395–437	416	153.7 ± 2.3
D^+	5	17	395–439	417	156.2 ± 2.1
D^+	6	15	401–437	419	156.2 ± 2.4
Recommended value					155.0 ± 1.6^b

[a] The errors are standard errors of the least-squares method.

[b] The recommended value is the average of the individual runs, $T = 405$ K the error is the 95% confidence interval for the mean.

2.2.2. [Ti(MDEA)(OC(C_2H_5)$_2$C(C_2H_5)$_2$O)]$_2$ (II)

The measurements were carried out in the temperature range 370–440 K. At $T = 428$ K and $U_{\mathrm{ioniz}} = 98$ V, the mass spectrum of the gas phase over II consists mainly of the following ions with the relative current intensities shown in parentheses: $[Ti_2(MDEA)_2O_2]^+ = A^+$, $m/z = 362$ (100%), $[Ti(MDEA)(OC(C_2H_5)_2)]^+ = B^+$, $m/z = 219$ (40%) and $[[Ti(MDEA)(OC(C_2H_5)_2C(C_2H_5)_2O)]_2\text{-}28\ \mathrm{Da}]^+ = C^+$, $m/z = 309$ (13%). The peak with the maximum mass-to-charge ratio corresponds to the $[[Ti(MDEA)(OC(C_2H_5)_2C(C_2H_5)_2O)]_2\text{-}28\ \mathrm{Da}]^+ = D^+$, $m/z = 646$ (3%).

Studies of the temperature dependencies of the ion currents $I(A^+)$ and $I(D^+)$ enabled the standard evaporation enthalpy of II to be determined by the second law method using the least-squares procedure (Table 2). The equation of the temperature dependence of the saturated vapor pressure of II can be written as follows:

$$\ln(p\,[\mathrm{atm}]) = 27.80 \pm 1.77 - \frac{18640 \pm 195}{T},\quad T = 370{-}440\,\mathrm{K}$$

3. Results and discussion

We have taken a structural–thermochemical approach to the experimental results in order to correlate vaporization enthalpies with the structures of the molecular coordination compounds. The method developed by us [2] is based on the determination of which atoms (or groups of atoms) within a complex, are the most important when considering intermolecular interactions. The central metal atom with its first coordination sphere and some of the other atoms making up the organic ligands may be shielded to a large extent due to the structural parameters imposed by the central atom. Structural and thermochemical reference parameters used in our approach are based on contributions to the evaporation enthalpy (liquid → gas transition) of organic substances [3]. Appropriate functional group types were chosen representing the types of intermolecular interactions present in this case. This assumes that the intermolecular interactions are not greatly influenced by the mobility constraints imposed by binding chemical groups to a central metal atom, and that electronic influences of the coordination complex on the peripheral groups are insignificant.

4. Locating atoms which contribute significantly to the intermolecular interaction

4.1. The calculation of the intermolecular contacts using X-ray structural analysis data

The estimation of intermolecular contacts of atoms in examined structures was performed using 'Platon' [4]. The effective radii of intermolecular interaction R_{eff} were taken from [5] (Table 3, variant 1). The condition for a contact: $d(\mathrm{I{-}J}) < R_{\mathrm{eff}}(\mathrm{I}) + R_{\mathrm{eff}}(\mathrm{J}) + 0.2$ Å, where d(I–J) is the distance between atoms I and J. This shows that only carbon–hydrogen fragments are involved in intermolecular interactions for I and II (Fig. 1a and b; Table 4).

Table 3
The effective radii of intermolecular interaction

Atom	C	H	N	O	Ti
R_{eff} (Å); variant 1	1.70	1.20	1.55	1.52	2.27
R_{eff} (Å); variant 2	1.25	0.95	1.25	1.30	1.70

4.2. The evaluation of possible intermolecular contacts for 'free' molecules

It was conducted through the use of the original program "Contact" [6]. The program manipulates two identical models possessing the structure corresponding to that of molecules in solid (gas) phase (Fig. 1a and b). Rotation by arbitrary angle (three consecutive revolutions around *x*, *y*, *z* axes) is followed by calculation of the shortest intermolecular contact distance (Table 4). 500 rotation—contact cycles (1000 contacts) were sufficient to identify the important interactions. In order that the calculation data can be related to those obtained earlier for other compounds, two sets of effective radii were used (Table 3). Variant 2 data (Table 3) were taken from atomic-molecular model calculations [7]. Both radii sets identified the same contacting groups.

4.3. Assessment of chemical group contributions to vaporization enthalpy by comparative shielding contributions of each atom or groups of atoms

The calculation was carried using the original program 'Sphere' [8]. which assesses the coordination capacity of a ligand in terms of the degree of filling of the coordination sphere around the central atom. This is calculated at given radial distance from the central atom (*R*) located at the origin of the coordinates.

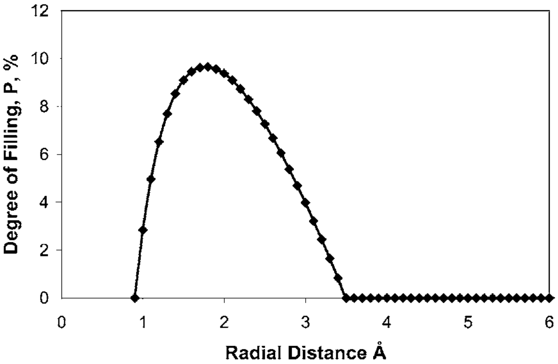


Fig. 2. Example demonstrating the degree of filling of the coordination sphere of a central point atom at the origin (*P*, %) by a single atom ($R_{eff} = 1.3$ Å) vs. the radial distance from it (*R*, Å).

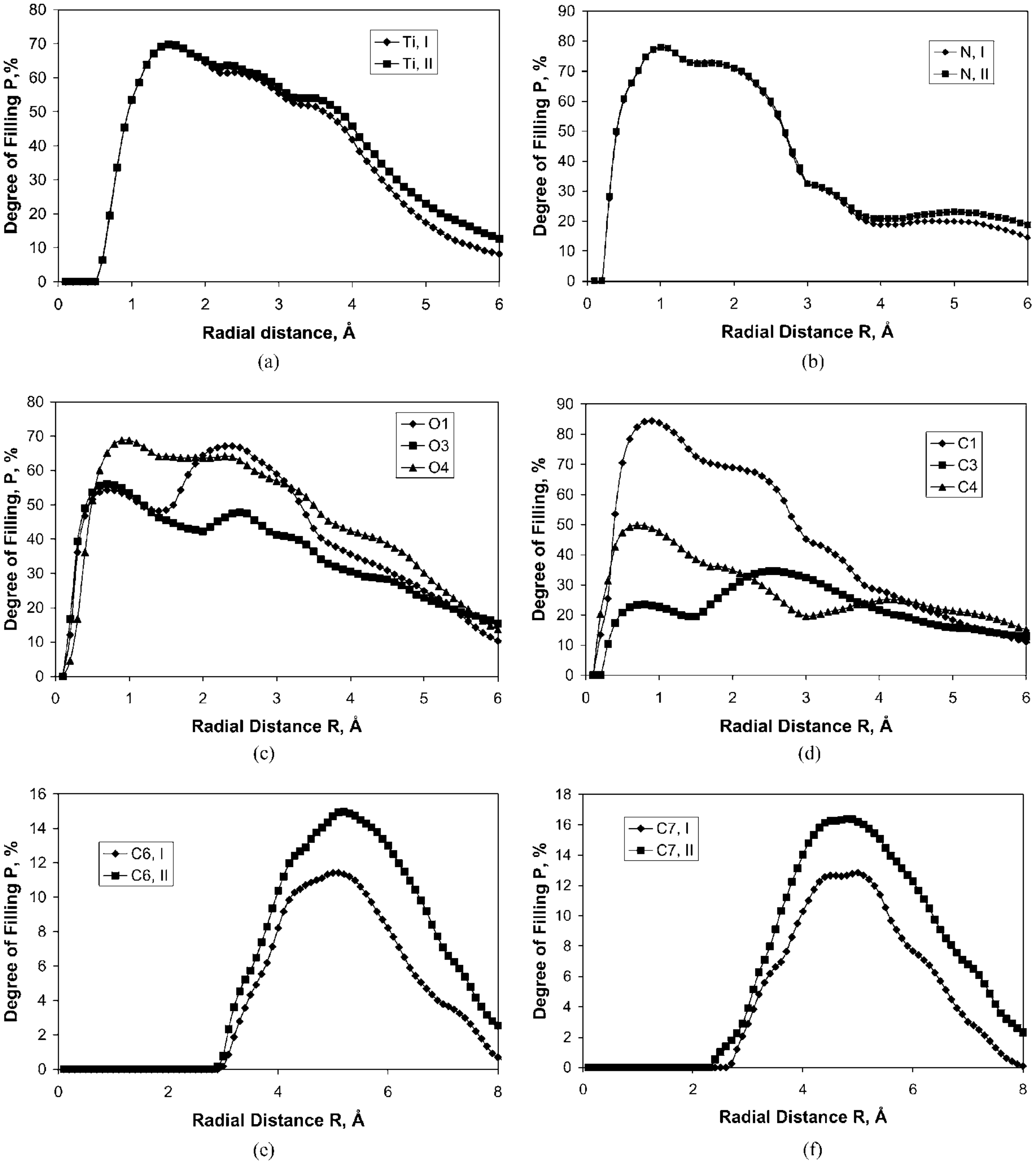
In this program atoms are considered as spheres with the effective radii suggested for atomic-molecular models (Table 3, variant 2) [7]. At specified *R* the degree of shielding of the central atom (*P*, %) can be computed from the formula: $P = (S/4\pi R^2) \times 100\%$, where *S* is the part of the surface of a sphere around the central atom (the radius is equal to *R*), occupied with atoms of ligands. Fig. 2 shows an example of the variation in of shielding of the central atom of a coordination compound by a single atom as a function of *R*. The area beneath the curve accounts for the specific volume of the coordination sphere.

Fig. 3 illustrate the *R*—dependence of the degree of shielding of various atoms and atomic groups in complexes I and II. Fig. 3a illustrates the high degree of shielding of titanium atoms. The similarity of the structures I and II lead to similar curves, particularly their coincidence at the oxygen region (the first peak). The environments of the nitrogen atoms exhibit the highest degree of shielding in the complexes under examination (Fig. 3b). This fact is consistent with the

Table 4
Atomic groups involved in intermolecular interaction in complexes I and II

Compound	Atomic group types	Group numbers[a] 'Platon'	Groups numbers[a] 'Contact'
I	(CH_3–)	9, 10, 11	3, 8, 9, 10, 11
	(–CH_2–)	4, 6	4, 5, 6, 7
II	(CH_3–)	3, 11, 13, 15	3, 9, 11, 13, 15
	(–CH_2–)	4, 8, 14	4, 5, 8, 12

[a] See Fig. 1a and b.



(a) (b) (c) (d) (e) (f)

Fig. 3. (a) The degree of filling of the coordination spheres of the titanium atoms in complexes I and II; (b) the degree of filling of the coordination spheres of the nitrogen atoms in complexes I and II; (c) the degree of filling of the coordination spheres of oxygen atoms O1, O3 and O4 of complex II; (d) the degree of filling of the coordination spheres of carbon atoms C1, C3 and C4 of complex II; (e) the degree of filling of the coordination sphere of carbon atom C6 in complexes I and II; (f) the degree of filling of the coordination sphere of carbon atom C7 in complexes I and II.

absence of intermolecular contacts (Table 4). The shielding curves of oxygen atoms illustrated by the example of II are also similar in shape (Fig. 3c). The bridging oxygen atoms O4 included in the MDEA chelate ring display the maximum shielding. The non-bridging oxygen atoms O3 of the MDEA chelate ring are shielded to a lesser extent. Atoms O1 and O2 of the chelating diolate are highly shielded but the maxima in the shielding curves are shifted to higher values of R compared to that for the O4 atom. This indicates that the free volumes of their coordination spheres are substantially higher, increasing the possibility of intermolecular interactions, although this is not realized in the solid state structures of I and II.

The terminal methyl groups exhibit the minimum degree of shielding, while as expected, the quaternary carbon atoms are the most highly shielded (Figs. 1a and b, and 3d). The (–CH_2–) groups of the MDEA cycle are shielded equally (Fig. 3d), however, the degree of shielding of (–CH_2–) groups 6 and 7 in II are higher than those of the similar groups in I as shown in Fig. 3e and f (for clarity only the carbon–hydrogen environment of the (–CH_2–) groups was taken into account in the calculations). This reflects the relative steric influences due to the mobilities in the carbon–hydrogen chains. The shielding enhancement (degree of filling of the coordination sphere) is large enough for the groups of interest to be excluded from intermolecular interactions.

5. Analysis of the experimental and theoretical values of vaporization enthalpies

Compound I. The intermolecular interaction results using "Contact" and "Platon" agreed closely, with the expected slight differences, "Platon" utilising only one solid state configuration. Thus, the pseudo-gaseous state calculation by "Contact" identified a greater number of atoms taking part in intermolecular interactions than that estimated by "Platon", with contacts involving carbon atoms 3, 5, 7 and 8 (Table 4). Although in the observed solid state structure there are no close intermolecular contacts, in the liquid and especially in the gaseous phases, the exposed methyl groups 3 and 8 as well as (–CH_2–) groups 5 and 7 interact with carbon–hydrogen fragments of neighbouring molecules. Both calculations show that the titanium, nitrogen and oxygen atoms do not participate in intermolecular interactions.

Compound II. As in the case of I, only carbon–hydrogen contacts were realized in the solid state structure (Table 4). The main distinction from I lies in the fact that (–CH_2–) groups 6 and 7 are totally shielded from intermolecular interactions due to the increased carbon–hydrogen periphery. However, these shielding groups are themselves involved in intermolecular interactions, resulting in a net increase in the intermolecular interactions.

All intermolecular contacts (Table 4) were taken into account for calculation of the evaporation enthalpies $\Delta_v H^\circ$, of I and II. The calculations of the evaporation enthalpy, $\Delta_v H^\circ$ (298 K) (liquid–gas transition) performed using the group contributions method with the scheme using the first environment only, are shown in Table 5. Benson–Buss group symbolism was employed [9,10] to identify the group types. Thus, the contributions 1.52 ± 0.05 kcal/mol for C–(C)$(H)_3$ groups, and 1.14 ± 0.01 kcal/mol for C–$(C)_2(H)_2$ groups were adopted. The contribution of C–(N)$(H)_3$ groups (C3 atom, Fig. 1a and b) was taken to be equal to that of C–(C)$(H)_3$ group. Assuming that $\Delta_v H^\circ$ does not vary significantly between the 298 K and the melting point, the melting enthalpy $\Delta_m H^\circ$ measured experimentally by DSC and DTA can be added to the theoretical magnitude of the evaporation enthalpy $\Delta_v H^\circ$ to give the theoretical value of the sublimation enthalpy $\Delta_s H^\circ$ at the melting point. Thus, the values of the sublimation enthalpies were calculated to be 143.8 ± 7.4 kJ/mol ($T = 518$ K) for I and

Table 5
The theoretical evaporation enthalpies of complexes I and II

Compound	No. of C–(C)$(H)_3$ groups	No. of C–$(C)_2(H)_2$ groups	$\Delta_v H^\circ$ (298 K) (kJ/mol)
I	10	8	101.8 ± 2.4
II	10	10	111.3 ± 2.5

Table 6
Comparison of calculated and measured sublimation enthalpies for complexes I and II[a]

Compound	$\Delta_v H^\circ_{calc}$ (298)	$\Delta_m H^\circ_{meas}$	$\Delta_s H^\circ_{calc}$	$\Delta_s H^\circ_{meas}$
I	101.8 ± 2.4	42 ± 5 ($T = 518$ K)	143.8 ± 7.4 ($T = 518$ K)	143.6 ± 1.8 ($T = 391$ K)
II	111.3 ± 2.5	46 ± 2 ($T = 450$ K)	157.3 ± 7.5 ($T = 450$ K)	155.0 ± 1.6 ($T = 405$ K)

[a] All values quoted in kJ/mol.

157.3 ± 7.5 kJ/mol ($T = 450$ K) for II. The melting points and experimental temperatures used in the mass spectrometer do not differ greatly and it is assumed that the value of $\Delta_s H^\circ$ will change very little between these temperatures. The theoretical and calculated values (Table 6) show a very close agreement. The errors are rather large due to the difficulties in measuring the melting enthalpies caused by the onset of decomposition just above the melting points.

6. Conclusions

A semi-empirical method for predicting sublimation enthalpies of volatile titanium compounds has been demonstrated. The close agreements between the measured and calculated sublimation enthalpies reveals the possibility of preselecting the volatility of titanium coordination compounds by subtle modifications in their structures. We aim to correlate their vaporization parameters with those of other (for example, barium) complexes in order to optimize stoichiometry control in multicomponent oxides.

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